

# Synthesis and Characterization of Novel Hydroxyl-Terminated N—N-Bonded Resins

K. SRIDHARA, S. R. JAIN

Propellant Chemistry Laboratory, Department of Aerospace Engineering, Indian Institute of Science, Bangalore 560 012, India

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**ABSTRACT:** Novel resins containing carbonyl or thiocarbonyl moiety; N—N bonds; etheral linkage; and terminal hydroxyl groups, that is, bis(bisvanillincarbohydrazone-4'-oxy)butane 1,4-diyl diether and bis(bisvanillinthiocarbonylhydrazone-4'-oxy)butane 1,4-diyl diether, have been synthesized by condensing bisvanillincarbo- and bisvanillinthiocarbonylhydrazones, respectively, with 1,4-dibromobutane. The resins were characterized by elemental and hydroxyl equivalent analyses, infrared and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, and other properties relevant to their use as propellant binders, such as calorific value, thermal analysis, viscosity, and burning rate measurements. Both these resins have convenient viscosity, indicating their suitability as binders for processing high solid loading, at slightly above room temperature. The resins could be cured easily with toluene diisocyanate and glycerol. The DTA-TG data show that the cured samples start to decompose exothermically at relatively low temperatures, in the range around 160°C. The resins ignite immediately on coming in contact with pure nitric acid, indicating their hypergolic nature. The burning rates of the ammonium perchlorate-based propellant compositions having these resins as binders are much higher than those processed with a conventional butadiene binder. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3204–3211, 2001

**Key words:** N—N-bonded resins; biscarbonylhydrazones; solid propellant binders; burning rate; hypergolic fuels

## INTRODUCTION

Polymers characterized by N—N bonds in their structures are of practical importance in a variety of applications and have been the subject matter of numerous investigations.<sup>1</sup> One of the latest developments in this area concerns the possible application of N—N-bonded polymers as energetic binders for powder compositions used in

solid and hybrid propellants,<sup>2–6</sup> because these have been found to enhance the burning rate of solid propellants and to reduce the ignition delay of the self-igniting (hypergolic) hybrid systems. To serve this purpose, however, telechelic prepolymers having specific chemical make-up to give high energy and mechanical strength, adequate viscosity for high solid loading, and suitable reactive end groups for curing are required. Besides, their curing reactions should not result in splitting of small molecules. Hydroxyl-terminated polybutadiene (HTPB) prepolymer, currently used in most solid composite propellants, has all these requisites and serves as an excellent binder.

Correspondence to: S. R. Jain (sambat@ aero.iisc.ernet.in).  
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In recent years, however, attempts have been made to make use of energetic binders to achieve higher specific impulse and also to enhance the burning rate of solid propellants. It is now well established that compounds having N—N bonds have superior ignition and combustion characteristics. Keeping this in view, a series of epoxy-terminated N—N—bonded resins were synthesized by Jain and coworkers<sup>7-9</sup> to serve as propellant binders. Hydroxyl-terminated polymers are preferred for binder applications because, on reacting with isocyanates, these polymers produce urethanes, which on curing form networks having excellent mechanical properties. However, viscous polymers based on N—N bonds that also have reactive hydroxyl groups have not been prepared so far. A survey of the literature reveals that the N—N—bonded polyethers synthesized by Hirose et al.<sup>10</sup> were solids at room temperature.

In this study, we report the synthesis and chemical characterization of two hydroxyl-terminated N—N—bonded resins, that is, bis(bisvanillincarbohydrazone-4'-oxy)butane 1,4-diyldiether (VCBE) and bis(bisvanillinthiocarbonylhydrazone-4'-oxy)butane 1,4-diyldiether (VTBE), which are found to be viscous fluids at room temperature. The resins were prepared for the first time by condensing 1,4-dibromobutane with bishydroxyl vanillincarbo- and bishydroxyl vanillinthiocarbonylhydrazone, respectively.

## EXPERIMENTAL

### Materials

1,4-Dibromobutane was prepared by reacting tetrahydrofuran (E. Merck, India) with 47% hydrobromic acid (S.D. Chemicals, India), according to the procedure described elsewhere.<sup>11</sup> A clear liquid (bp 62°C) obtained, was characterized by its <sup>1</sup>H-NMR spectrum, which showed two resonances at  $\delta$  2.03 and 3.45 ppm downfield tetramethylsilane (TMS), attributed to the core and flanked CH<sub>2</sub>, respectively, of the dihalide.

Carbohydrazide and thiocarbohydrazide were prepared as previously reported.<sup>12,13</sup> Bisvanillincarbohydrazone (VCH) and bisvanillinthiocarbonylhydrazone (VTCH) were synthesized by refluxing ethanolic solutions of vanillin (BDH, India) and carbohydrazide or thiocarbohydrazide,

as described previously.<sup>12-14</sup> The purity of these compounds was ascertained by comparing their melting points and <sup>1</sup>H-NMR spectra with those reported previously.<sup>14</sup>

### Preparation of Resins

#### VCBE

A solution of VCH (0.126 mol) in dimethylformamide (DMF) and 1,4-dibromobutane (0.106 mol) were refluxed at 120°C for 20 h in the presence of sodium carbonate. The red-brown mixture formed was shaken with chloroform. The chloroform layer was separated and washed with water to remove DMF. After drying over anhydrous sodium sulfate, the chloroform was removed on a rotary flash evaporator. The red-brown viscous resin was obtained in about 90% yield.

#### VTBE

The resin was synthesized by following an analogous procedure. The reflux time in this case was 10 h. The yield of the orange-red viscous resin obtained after removal of chloroform was over 70%.

### Characterization

The carbon, hydrogen, and nitrogen elemental analysis was carried out on a Heraeus microanalyzer (Heraeus, Hanau, Germany). The hydroxyl equivalents (mequiv/g of the resin) of the two resins were determined titrimetrically, after the acetylation of the hydroxyl groups using acetic anhydride-pyridine mixture, as described elsewhere.<sup>15</sup>

The infrared spectra of the polyethers were recorded as neat samples on a Perkin-Elmer 781 infrared spectrometer (Perkin-Elmer, Palo Alto, CA).

The <sup>1</sup>H-NMR spectra of the starting compounds were recorded on a Varian T-60 instrument (Varian Associates, Palo Alto, CA) using DMSO-*d*<sub>6</sub> as solvent, whereas those of the resins were obtained on a WH-270 Bruker FT-NMR machine (Bruker Instruments, Billerica, MA), in CDCl<sub>3</sub>, using TMS as the internal standard. The <sup>13</sup>C-NMR and spin echo Fourier transform (SEFT) NMR spectra were recorded on an AMX-400 instrument, using CDCl<sub>3</sub> as solvent.

A Shimadzu gel permeation chromatograph (Shimadzu, Japan) was used to estimate the mo-

lecular weights of the resins, after calibrating with polystyrene of known molecular weight.

The viscosity measurements were carried out on a T-spindle Brookfield rotation viscometer (Brookfield Engineering Inc., USA), in the temperature range 30–60°C.

Simultaneous TG-DTA thermograms of the resins were recorded on a DT-40 Shimadzu thermal analyzer, at a heating rate of 10°C/min, in flowing nitrogen atmosphere, using a sample of about 10 mg.

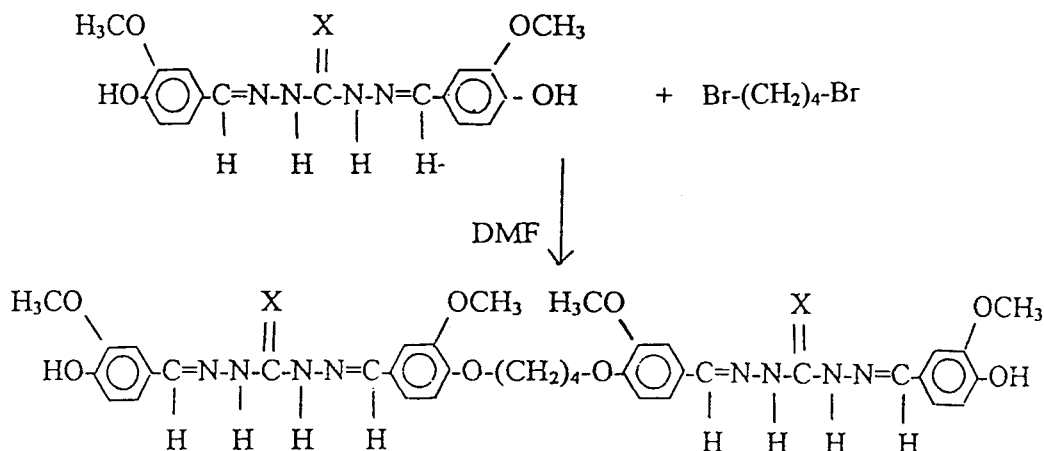
The heats of combustion of the neat and cured resin samples were determined using a Toshni-

wal combustion bomb calorimeter (Toshniwal Instruments, India), which was calibrated with benzoic acid.

## RESULTS AND DISCUSSION

### Synthesis

The reaction between bisvanillincarbo- or bisvanillinthiocarbonylhydrazone with 1,4-dibromobutane could be described by Structure 1:



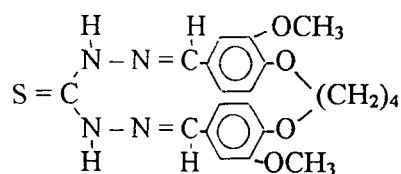
Structure 1

where VCBE is represented when X = O and VTBE is represented when X = S.

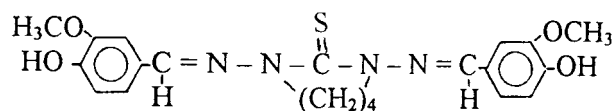
The carbon, hydrogen, and nitrogen elemental analyses of the two resins, given in Table I, approximate those calculated for the products depicted in resin Structure 1.

The hydroxyl equivalent values of the two resins are also close to those expected for the proposed structure. The GPC of VTBE clearly shows a broad peak in the molecular weight range 763–972, which corresponds to the resin formula weight (802), as expected from Structure 1, in the reaction scheme. Apparently, the higher polymeric species are not formed under these reaction conditions. On the lower molecular weight side, however, another peak is shown, which corresponds to molecular weight 410. This could apparently be attributed to cyclic products formed

by the simultaneous dehydrobromination of the two O—H or possibly the two N—H protons, as shown in Structure 2 and Structure 3 (formula weight 428):



Structure 2



Structure 3

**Table I** Elemental Analysis and Hydroxyl Equivalent Data

Resin	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Hydroxyl Equivalent (mequiv/gm)	
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
VCBE	58.50	59.22	6.17	5.45	11.11	14.55	2.3	2.6
VTBE	56.95	56.86	6.10	5.24	12.71	13.96	2.4	2.5

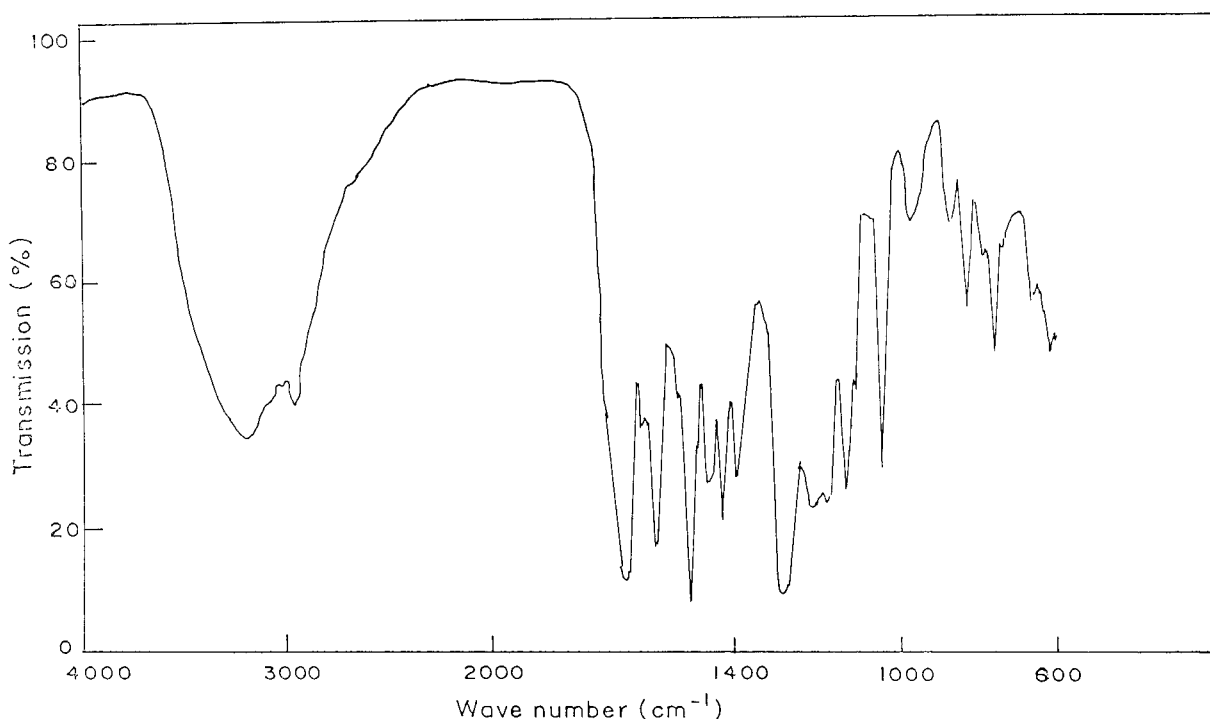
The slight discrepancy observed in the elemental analysis could perhaps be related to the presence of the cyclic species, the amount of which could be as high as 20%. However, the main product appears to be the one as shown by Structure 1, in the reaction scheme.

### Spectral Characteristics

The infrared spectrum of VCBE, given in Figure 1, shows all the major absorption peaks expected from Structure 1. Strong absorption in the region 3300–3100  $\text{cm}^{-1}$  could be attributed to the presence of O—H and N—H bonds. The C=O absorption appears as a shoulder at 1700  $\text{cm}^{-1}$  merged with C=N, which peaks at 1660  $\text{cm}^{-1}$ . The other recognizable absorption bands are at 2900  $\text{cm}^{-1}$ ,

attributed to the azomethine (NC—H) group; at 1270 and 1120  $\text{cm}^{-1}$ , attributed to N—N; and at 1020  $\text{cm}^{-1}$ , attributed to ether (C—O—C) linkage. The IR spectrum of the thio-analog resin (VTBE) is similar to that of VCBE, except that the shoulder at 1700  $\text{cm}^{-1}$ , attributed to C=O, is absent.

The  $^1\text{H}$ -NMR spectrum of VTBE (Fig. 2) shows all the expected resonances and could be assigned easily by comparing with those of the parent compounds.<sup>14</sup> The butyl group resonances appear at  $\delta$  [given as ppm (intensity)] 2.13 (0.6) and 2.86 (4.5), attributed to the core and the flanked  $\text{CH}_2$  protons, respectively. The flanked proton resonances appear substantially upfield compared to those in the dibromide, as expected. The methoxy and the

**Figure 1** Infrared spectrum of VCBE.

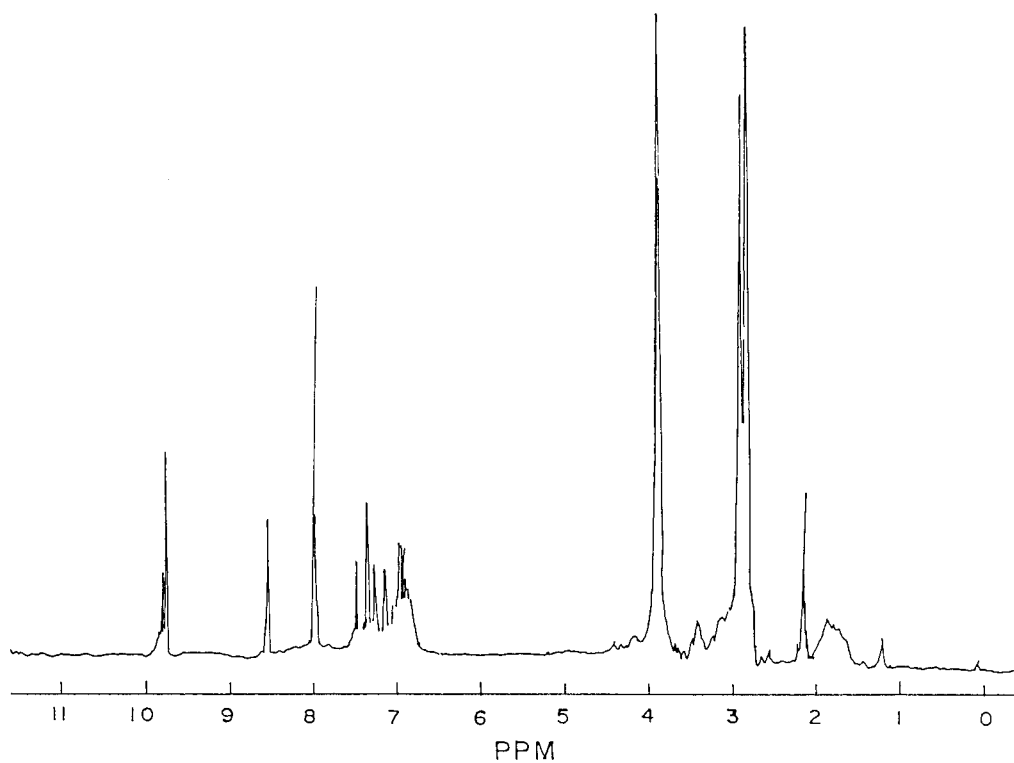


Figure 2 <sup>1</sup>H-NMR spectrum of VTBE.

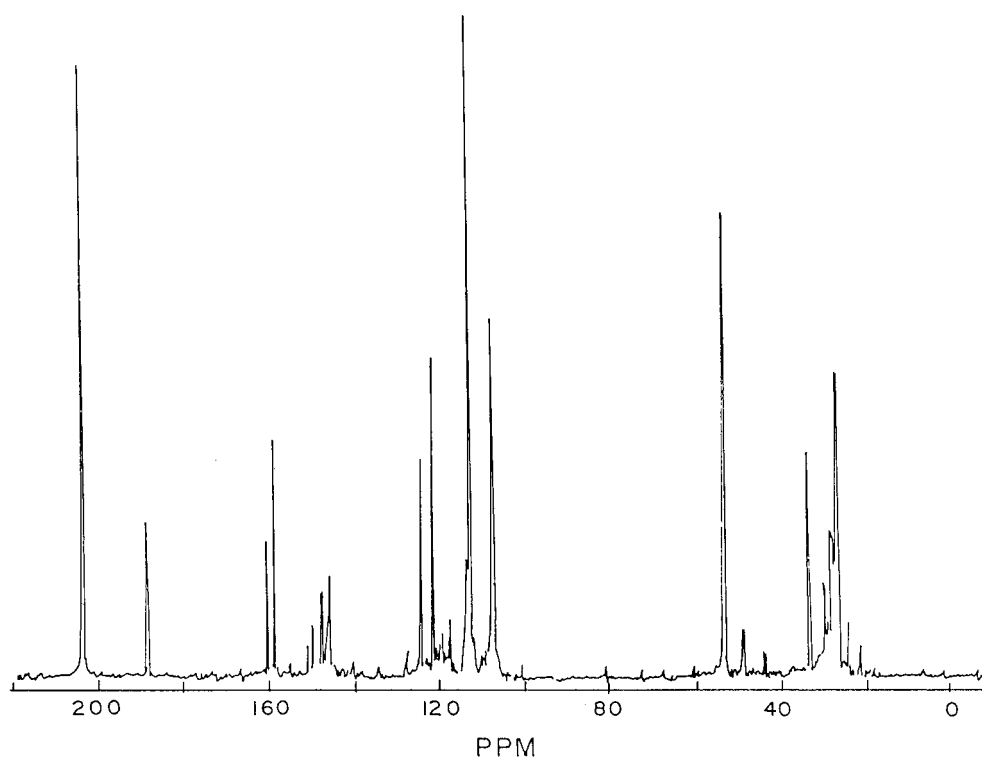


Figure 3 <sup>13</sup>C-NMR spectrum of VTBE.

azomethine (N=CH) proton resonances appear at  $\delta$  3.89 (5.8) and 7.95 (1.9). The aromatic protons appear in the range  $\delta$  6.9 to 7.5 (5.8), as reported for VTCH.<sup>14</sup> The resonances at  $\delta$  8.54 (0.3) and 9.76 (0.56) are attributed to the OH and NH protons. These appear substantially upfield compared to those in VTCH. The ratio of the intensity of OH to NH protons is closer to 1 : 2, indicating that two of the hydroxyl protons of the two hydrazones are used up in the course of dehydrobromination and condensation process with 1,4-dibromobutane. The <sup>1</sup>H-NMR spectrum of VCBE is almost identical to that shown for VTBE in Figure 2.

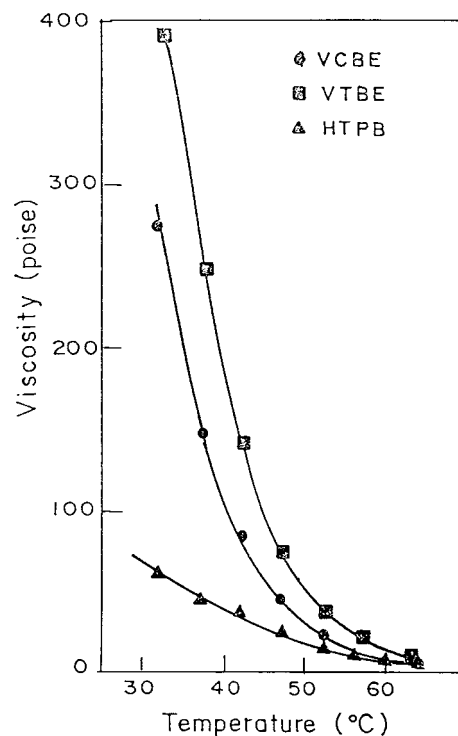
The proton broad-decoupled <sup>13</sup>C-NMR of VTBE (Fig. 3) reveals resonances at  $\delta$  28.4 (3.63) and 33.5 (5.49), which correspond to the aliphatic carbons of the butyl group. The resonance at  $\delta$  53.4 (11.15) is attributed to the methoxy carbon. The aromatic carbons of the vanillin moiety are seen at  $\delta$  124.1 (5.45), 107.8 (8.77), 146 (2.46), 158.7 (5.84), 113.2 (16.06), and 121.6 (7.83). The thionyl carbon resonance occurs at  $\delta$  188.4 (3.91), whereas the azomethine carbon appears at  $\delta$  204 (14.96). In vanillin, the aldehyde carbon appears at  $\delta$  192 ppm.<sup>16</sup> To assign the azomethine carbon resonance unequivocally a SEFT spectrum was taken. The SEFT spectrum shows a reverted peak at  $\delta$  204, thus confirming that this peak is attributed to the azomethine carbon. The only other peak reverted at 27 ppm in the SEFT spectrum is attributed to CHCl<sub>3</sub>, present as an impurity in CDCl<sub>3</sub>, used as solvent. The <sup>13</sup>C-NMR spectrum of VCBE was found to be identical to that of VTBE. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectral data thus agree well with the resin structure as depicted in Structure 1.

### Physical Properties

These resins are orange-red color viscous fluids at room temperature, soluble in common polar sol-

**Table II Heat of Combustion, Viscosity, and Density Data**

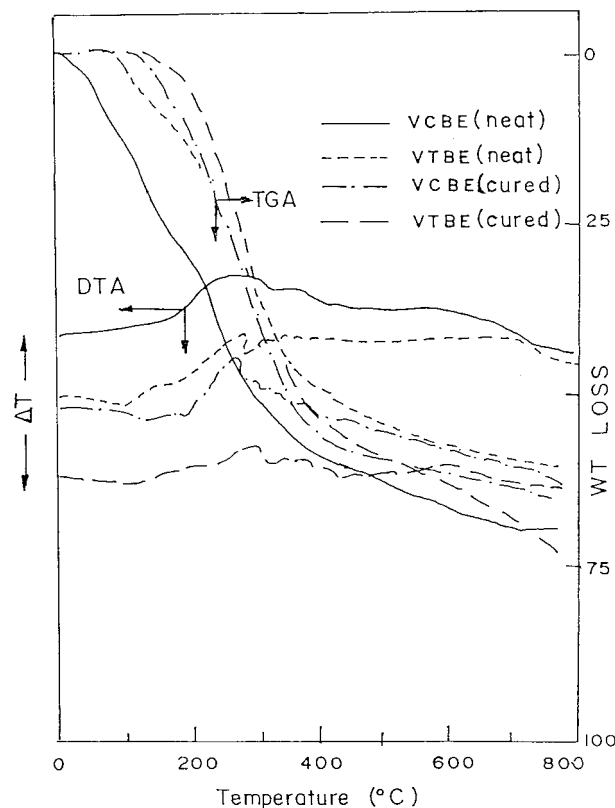
Resin	Viscosity (poise)	Heat of Combustion (kcal/gm)		Density (g/cc)
		Observed	Calculated	
VCBE	140.0	6.20	6.30	1.18
VTBE	240.0	6.30	6.40	1.20



**Figure 4** Variation of viscosity with temperature.

vents. The heat of combustion, viscosity at 35°C, and density at room temperature are given in Table II. The viscosity decreases sharply with an increase in temperature, as shown in Figure 4. In comparison to the viscosity variation of HTPB, the increase is rather steep on lowering the temperature. However, at slightly above room temperature, the viscosity is comparable to that of HTPB, and thus is suitable for processing high solid loadings, which are desired in solid propellants. The densities of the resins are also high. The experimental heats of combustion compare well with those calculated by the method developed by Jain.<sup>17</sup>

The resins were cured using toluene diisocyanate linearizer, assuming the resin formula according to Structure 1. Thus a composition comprised of the resin (61.6%), toluene diisocyanate (28.4%), glycerol crosslinker (5%), and dimethyl sebacate plasticizer (5%) was cured at 80°C for 3 days. The cured samples were solid materials, believed to be fully cured; however, the exact degree of curing was not determined. The samples were characterized by TG and DTA for thermal stability. The same cure composition and procedure for curing was used for casting propellant



**Figure 5** DTA-TG thermograms of the neat and cured resins.

samples, which had 70% ammonium perchlorate (AP) loading.

The simultaneous DTA-DTG data show that the resins decompose exothermically (Fig. 5), as expected for N—N—bonded compounds.<sup>18</sup> They start losing weight slowly above 90°C, which could be because of evaporation; rapid decomposition occurs above 160°C, as indicated by the onset of exotherm in the DTA and rapid weight loss in TG thermograms. The decomposition exotherm peaks around 220°C. Apparently, VTBE decomposes slowly. At 300°C, the weight loss is 60 and 40% for VCBE and VTBE, respectively.

The decomposition of the cured resins begins around 170°C and follows a pattern similar to that of the neat resins. The weight loss is rapid in the range 200–400°C. Over 65% weight is lost at 400°C. Above this temperature, the decomposition slows down; the weight loss corresponds to about 70% at 750°C. The thermograms of the cured samples bear close resemblance, with no noticeable difference in their decomposition patterns. As expected, the cured VCBE decomposes

slower than does the neat sample. The somewhat faster rate of decomposition of the cured VTBE compared to that of the uncured sample in the high temperature range is rather puzzling. It could be the result of incomplete curing because the noncrosslinked urethane formed might degrade faster. The occurrence of decomposition at relatively low temperatures with some amount of exothermicity is a feature desired for their application as binder in solid propellants.

### Combustion Characteristics

One of the interesting properties of these resins is that they ignite spontaneously (hypergolic) on coming into contact with liquid oxidizers, such as white fuming nitric acid (WFNA). The ignition delay with WFNA of these resins was of the order of 800 ms, determined using a drop tester-type device described elsewhere.<sup>19</sup> The hypergolic nature of the N—N—bonded compounds, previously established,<sup>2,13</sup> if present in a polymeric resin, is a desired feature when considering it as a binder for hypergolic solid fuels used in hybrid rockets.

The AP-based propellant strands, processed with the new resin binders (VCBE and VTBE), were cured and coated with a slurry of TiO<sub>2</sub>. The linear burning rate, an important parameter of solid propellants, was determined using a strand burner, as described earlier,<sup>4,6</sup> under nitrogen pressure (70 atm). The burning rates of the AP propellants were found to be 11.35 and 11.0 mm/s, respectively, with the VCBE and VTBE resins, which are almost double that obtained (5.5 mm/s) with the often used carboxyl-terminated polybutadiene (CTPB) binder, with the same (70%) AP solid loading. It is thus clear that using these resins as binders could enhance the burning rate of the solid propellants. These results parallel those obtained earlier in our laboratory with other N—N—bonded resins.<sup>3–6</sup> The higher burning rate is apparently related to the high reactivity of the N—N—bonded binders with HClO<sub>4</sub>, the primary product of AP decomposition.

### CONCLUSIONS

Bisvanillincarbo- and bisvanillinthiocarbonylhydrazones on condensing with 1,4-dibromobutane yield N—N—bonded hydroxyl-terminated resinous products. The resins have suitable viscosity around room temperature to process high

loading of powder compositions. The resins ignite immediately on coming into contact with liquid oxidizers like WFNA, a property that could be useful for considering them as binders for hypergolic hybrid propellant fuels. The AP-based solid propellants processed with these resins as binders have higher burning rates than those having the usual polybutadiene resins.

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